

Kinetics of Formation and Absorption Cross Section of the ClO Dimer

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The technique of Flash Photolysis with UV Absorption Spectroscopy has been used to study the formation of Cl₂O₂ from the self-reaction of ClO radicals. Three separate monochromator / PMT absorption channels were used to follow the time-dependent evolution of both ClO and Cl₂O₂. ClO radicals were quantified using the differential spectroscopy technique, via simultaneous measurement of the ClO absorption at the (12,0) band peak and the adjacent valley of the (AX) transition at approximately 275nm. The concentration of ClO could thus be unequivocally determined in the presence of other absorbing species. The third detection channel was used to monitor the formation of Cl₂O₂ at lower wavelengths. Kinetic fitting to the ClO decay permitted comparison of the calculated yield of Cl₂O₂ with that measured using literature dimer cross sections. Experiments were performed over a range of conditions (temperature, pressure) relevant to the middle atmosphere, and the results obtained are compared with those from other recent laboratory studies.
